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(54) **Title:** COPPER-BASED FUNGICIDE AND BACTERICIDE AGENTS AND USE THEREOF

(57) **Abstract:** A copper-based fungicide and bactericide agent, suitable for direct foliar use in agriculture, soil treatment and pre-transplant direct buld dipping, enables an optimum transfer of copper to the treated varieties with an extremely low environmental impact, and made of amino acids or peptides or of mixtures thereof obtained from waste or products of animal, vegetal origin or obtained by synthesis or fermentation with an effective quantity of copper.

"COPPER-BASED FUNGICIDE AND BACTERICIDE AGENTS AND USE THEREOF"

DESCRIPTION

The present invention relates to a copper-based fungicide and bactericide agent, of a type commonly used in agriculture, for foliar use as well as for soil-directed treatments or by pre-transplant bulb dipping.

It is a well-known phenomenon that crops can be infested by various diseases of bacterial and/or fungal type.

To the state of the art belong fighting methods against such diseases, using chemical products of various types and compositions, synthetic or of mineral and/or vegetal origin, performing their action according to different mechanisms.

Among such fungicide and bactericide products of the state of the art, salts and other copper compounds like sulphates, oxychlorides, hydroxides, protoxides, and the like, besides the widely popular Bordeaux mixture, i.e., copper sulphate reacted with lime, are known. Said agents represent an important group, effective in the fight against infesting fungal and bacterial phenomena

These known copper-based products entails several drawbacks, among them:

* They can, anyhow, control merely a limited number of fungal and bacterial diseases;
* They are so-called 'covering' products, as they act without entering vegetal tissues with a translaminar action;
* They are used at high dosages, with the entailed high residual metal quantities onto the treated cultures, considering that copper ion is toxic to man and animals;
* They markedly pollute soils underlying cultures repeatedly treated within the agricultural year and over the years;
* produce a consequent in-soil accumulation with possible injurious effects towards the soil microflora and fauna;
* They cause a possible percolation into the water-bearing strata with the danger of polluting potable waters; and
* They negatively affect the agricultural produce and the processes for the treatment thereof, e.g., on must fermentation, being injurious to yeast when remaining in elevated residual quantities.

An idea of solution of the technical problem represented by said drawbacks stems from the fact that, besides the agents of the abovementioned type, the use of amino acids and peptides, only with regard to their nutrient and bio-stimulating action on cultures, is also known in agriculture. An example of such agents is disclosed in US 4,216,143 (Ashmead).

The possibility of mixing the amino acids and the peptides to the mineral micronutrients to increase the effectiveness or the persistence thereof is also well-known and widely used, since metallic salts are easily chelated or complexed by the peptides and the amino acids, thereby easing the entering thereof inside vegetal tissues.

In fact, thus the metal abandons the usual penetration pathway via a 'cationic' mechanism, rather, it being bound to the amino acids and losing its cationic feature, entering via the membrane crossing mechanism which is typical of amino acids and peptides; i.e., with a so-called 'smuggling' effect.

The technical problem underlying the present invention is that of providing an agent allowing to overcome the drawbacks mentioned with reference to the state of art.

This problem is solved by an active copper-based fungicide and bactericide agent, characterised in that it comprises amino acids or peptides or a mixture thereof obtained from waste or from products of animal, or vegetal, or synthetic origin, having an effective quantity of copper.

The latter may be provided, by mere way of example, from one of the following copper compounds: sulfates, more or less hydrated; oxychlorides; oxysulphates; hydroxides; oxydes; Bordeaux mixtures, etc., or from a mixture thereof.

For 'effective quantity' is meant a quantity useful to exert a bactericide and fungicide action.

Preferably, but not exclusively, as mixtures of amino acids and peptides, products deriving from the hydrolysis of protein-rich natural organic substances, e.g., those deriving from hide processing, with a <2000 dalton average molecular weight, such as to ease an optimal copper penetration into the vegetal substrate, may be used.

The main advantage of the agent according to the present invention lies in allowing an optimal transfer, to vegetal substrates, of effective copper amounts.

In fact, in the light of the abovementioned phenomenon of greater and quicker penetration, it has been devised to exploit the mechanism using copper rather as a fungicide and bactericide agent of easy penetration and no more solely for a foliar covering. Thus, moreover, the copper dose being reduced for a greater and quick penetration thereof, the abovementioned drawbacks are also sensibly reduced, and, in particular, the important problem of the environmental impact of copper.

Moreover, it has surprisingly been found that the greater ease of penetration of the copper ion-based compounds and amino acids and peptides enables a copper activity not merely against the diseases traditionally controlled therefrom, but also against fungal and/or bacterial diseases usually not copper controllable, as well as application techniques usually not viable with the traditional cupric products, like a

direct pre-transplant bulb dipping.

Hence, with respect to the state of the art, use of sole copper inorganic salts is dismissed in favour of that of copper ion complexed and chelates with amino acids or peptides or mixtures thereof, used onto the crops with a fungicide and bactericide effect becoming apparent at copper dosages which are markedly inferior to those traditionally used.

Therefore, these could represent a novel alternative in the control of the fungal and bacterial diseases of the crops, also in light of the fact that copper, though in use for more than a century, has never yielded resistance phenomena, mainly due to the multi-site activity thereof.

The present invention will hereinafter be described according to some preferred embodiments thereof, together with some preferred applications thereof, given by way of example and without limitative purposes with reference to the following examples.

The compositions constituting the fungicide and bactericide agents according to the present invention can have the following properties:

i. can be in a liquid, as well as in a powdery formulation;

ii. contain copper ion, preferably bivalent and in form of salt of the peptides and of the amino acids or in form of complex and chelated therewith, at concentrations ≤40% p/w, preferably ≤20% p/w;

iii. contain copper ion, preferably bivalent and in form of mixtures of copper organic and/or inorganic salts, e.g., hydroxides, copper oxides, copper sulphate in a mixture with amino acids or peptides or mixtures thereof containing the copper ion in form of salt of the peptides and of the amino acids or in form of complex or chelated therewith;

iv. the amino acids and the peptides are of natural origin, as, e.g., deriving from hydrolysis of waste or of protein-containing products of animal and/of vegetal origin, optionally charged with individual free amino acids or mixtures thereof, even of synthetic or fermentative origin;

v. the amino acids or the peptides or the mixtures thereof can derive from waste or from products of animal origin, or can be of synthetic or fermentative origin;

vi. the 22 natural amino acids, free as well as associated in more or less long peptide chains, the latter, preferably yet not essentially, having a <2000 dalton average molecular weight, may be provided;

vii. preferably, yet not essentially have a complete in-water miscibility and/or solubility; and

viii. have a pH, in a 10% solution, preferably ranging from 2 to 9.

The fungicide and bactericide agents as hereto identified have a wide range of possibilities as to the distribution thereof in agricultural sites.

Preferably, the latter can occur via the leaves or by soil treatment, or by pre-transplant direct bulb dipping.

Moreover, it should be highlighted that the fungicide and bactericide agents according to the present invention find use in the specific field of the integrated and biological fight to pests, since this type of fight foresees the application of sole copper-based fungicides or of sulphur.

The preferred application modes of the fungicide and bactericide agent are: foliar; dissolved into the irrigation waters; by pre-transplant bulb dipping; or according to the criteria of the integrated and biological fight.

Examples of application

Hereinafter, examples of application of the fungicide and bactericide agents according to the present invention are provided.

A) Production of the solution to be used

By way of example, to attain the solution to be used in practice a quantity of the agents is water-dissolved in a concentration ranging from 0.05% to 10% (from 50 g to 10 kg in 100 dm^3 water). The aqueous solution thus attained can be directly used onto the crops.

B) Foliar application.

The aqueous solution of the fungicide and bactericide agents according to the present invention is put in a suitable sprayer, which may be for hothouse crops, normal or automatic, with a piston pump, a preventive pressure pump, an air convection pump, and the like.

For open field crops, instead, nozzle-provided bar dispensers, autonomous or tractor-towed atomisers, preventive pressure pumps, air-conveying atomisers and the like are suitable.

Using these apparatuses, the leaves of the crops are carefully treated with the solution to attain a protection from the attacks of the fungal or bacterial diseases or to reduce the virulence of the latter.

C) In-soil treatments.

The aqueous solution of the fungicide and bactericide agents according to the present invention is let in apparatuses of the above described type. Using such apparatuses the soil is carefully sprayed, drenching it thoroughly, around the plants of the crops to be protected from fungal and/or bacterial diseases. Upon application, either a grounding of the product by light harrowing or milling of the soil, or a suitable

watering of the latter to let the product penetrate, is provided.

D) Treatments by direct bulb dipping

To fight the insurgence of specific fungal diseases onto the surface or inside of bulbs of floral and vegetable crops, the aqueous solution of the fungicide and bactericide agents according to the present invention is used by dipping bulbs therein for appropriate times (according to the type of bulb) so that it be adsorbed by the latter. Then, bulbs are sown (transplanted) into the soil.

* * *

Hereinafter, examples of use of the fungicide and bactericide agents according to the present invention are reported, and the obtained results evaluated.

Experimental tests

Example 1

A testing was conducted on ornamental crops (*Poinsettia*, Primrose, Gerbera, etc.), against different diseases: copper (Cu) concentrations were varied during the initial tests,.

Optimum doses were set at from 2 to 8 g/dm^3 for a copper content of about 5%; from 0.5 to 1.0 g/dm^3 for a copper content of about 7% for foliar use; and about 5 g/dm^3 for an in-soil use, adopted for the Poinsettia.

The assayed crops were: Chrysanthemum, Poinsettia, *Pothos*, Primrose, Gerbera, Geranium and *Impatiens* balsam. Then, the aromatic *plants*: Mint, Tarragon (*Artemisia*), Pot marigold, Borage, Lemon balm were tested.

Subsequently, the tests were repeated on Poinsettia, Primrose, Gerbera; moreover, tests were conducted on: Geranium, four varieties of Rose (in a hothouse) and Butterbush. Since not all the expected diseases occurred, hereinafter merely the crops wherein a disease developed onto the untreated theses are reported.

Poinsettia: 5 treatments at a 20-day interval with *Pythium ultimum* as pathogen. A 40.5% plant mortality was recorded in the untreated thesis, versus a 0.0% plant mortality in the treated thesis. Moreover, in foliar treatments a slight phytotoxicity was recorded, whereas the thesis with in-soil application exhibited an excellent appearance. In the subsequent test: 0.0% mortality in the treated theses versus a 33.3% in the thesis treated with a chemical-type product.

Primrose: 3 treatments every 20 days with *Botrytis* cinerea as pathogen. No attack on foliar-treated theses, and a 13% plant mortality with in-soil treatment were recorded, versus a 57% and a 23% mortality, for the untreated thesis and for a thesis treated with a chemical product (benomyl), respectively. Moreover, no phytotoxicity was recorded. Subsequently, with 6 treatments, a light phytotoxicity was found in theses treated with a 5% Cu agent, at 4 and 8 g/dm^3 water.

Gerbera: 3 treatments with *Phytophtora cryptogea* as pathogen were conducted. The 28%, 50%, 35% and 14% of mortality in the treated theses, versus the 50% and the 56%, respectively, for the chemical treatments (furalaxyl, tolchlofos methyl, benomyl) and the untreated thesis were recorded.

Tarragon: 4 treatments every 15 days, with *Puccinia dracunculina* as pathogen, were conducted. Infection ratios statistically not diverging from the chemical control (penconazole), yet significantly distinct from the untreated thesis, with a light phytotoxicity exclusively in the higher dosage theses, were detected.

Mint: The same treatments provided for Tarragon, with *Puccinia menthae* as pathogen, were conducted: an infection ratio inferior to that of the untreated thesis, yet not statistically significant, was recorded.

Sword lily and Lily bulbs: artificially infecting the bulbs with *Fusarium oxysporum* the following was attained: for Sword lily: curing for 20 minutes with agents comprising 5% and 7% Cu and with a mixture of control chemical products. At the higher doses, the agents are statistically indistinguishable from the chemical control, whereas both differ from the untreated, healthy and non-inoculated theses. In Lily the disease did not develop due to the avirulence of the deuteromycetes strains, however it was observed that the 5% and the 7% Cu agents do not cause phytotoxicity.

Rose: phytotoxicity is instead apparent in treatments with both products on roses. In the test set out on four hothouse varieties the Scab (*Marssonina rosae*) pathogen failed to develop. Treatments conducted onto the same varieties in autumn caused no phytotoxicity. The action of the two products on Butterbush *Fusarium oxysporum* was highly significant and effective: three foliar treatments with 5% Cu and from 4 to 8 g/dm^3 H_20, and with 7% Cu in 1 g/dm^3 water yielded results not statistically different from the standard chemical product (benomyl). 7% Cu in 5 g/dm^3 H_20, distributed in soil, yielded the best protection, with a positive effect of vegetation stimulation, as had also been observed for Poinsettia.

Example 2

Two experimental tests against Grape mildew, set out according to the existing norms for the plant protection product registration, were conducted.

Muscat grape: the doses adopted varied during the testing from 1000 to 9000 g/ha of 5% and 7% Cu agent, then with Cu doses ranging from 1/5 to 1/4 of the Cu content of the traditional reference product. Doses were increased after the first treatments, which were prudentially kept very low for fear of toxicity. The results show that in all cases the assayed products yielded statistically significant differences with respect to the untreated thesis. The addition of a wetting agent improved effectiveness. The observation of an optional effect on *Botrytis* as well highlighted a positive effect of

two of the treatment theses, with respect to the untreated thesis and to the traditional cupric reference product. Hence, the use of the agents is proposable in view of a biological agriculture or in an integrated fight with applications starting from after the setting.

Merlot grape: the effectiveness of the agents used, at the doses of 5-25 g Cu/100 dm3 H_20, equalled that of the standard reference product. Moreover, even a certain effect against *Botrytis* was detected, thus confirming observation in the abovedescribed tests on Muscat grape and Primrose. Therefore, the conclusion was that the 5% and 7% Cu agents, with Cu concentrations reduced to a 1/5 ratio with respect to those usually used, can replace the traditional cupric products. The test was repeated on Dolcetto grapes using 5% Cu agents at 3 and 6 kg/ha, 7% Cu agents at 1 and 2.5 kg/ha with 12 applications and also adding other two theses with less applications, i.e., starting only after setting, whereas the initial treatments were conducted with traditional fungicides. This was done in order to reduce the phytotoxic effects, which appear just in the early stages. A satisfactory control of Plasmopara viticola was found for all products, with a lesser effectiveness at lower doses. Since in the initial stages the examined products are less effective than the traditional fungicides, whereas they effectively protect in the final stages of the crops, it is advisable to adopt a varied strategy, with traditional fungicides in the first stages, subsequently reverting to the agents according to the invention.

Example 3

Tests on Apple, against scab, and on Tomato, against downy mildew, were conducted. Further tests were conducted against Grape mildew using agents according to the invention mixed with sulfur (Thiovit). There were seven treatments with 0.3% dosage (300 g/100 dm^3 ~ ca. 17 g Cu /100 dm^3). No phytotoxicity symptoms were observed. The test was repeated on Chasselas grapes using 5% Cu agent at 0.3 and 0.6% doses, and 7% Cu agent at 0.1 and 0.2% doses, as compared to other cupric products with nine treatments. The two higher-dose theses yield a satisfactory protection against downy mildew, showing, however, phytotoxicity symptoms. The lower doses maintain their effectiveness, though at a reduced level, exhibiting low phytotoxicity. The quantity of Cu distributed is unequivocally much lower and therefore more environmentally compatible. A test was conducted on Italian Riesling grape, in comparison with several other fungicides. The attack of the disease was especially virulent due to frequent precipitation. 6 treatments were conducted with 0.3% agents, yielding the following results with respect to the control thesis and to the standard cupric product: Rate of infection on grapes (effectiveness %): 16.8 (76.3%), versus 83.5 and 12.6 (84.9%); Rate of infection on leaves

(effectiveness %): 9.6 (88.6%), versus 84.3 and 10.3 (87.8%).

Example 4

Tests analogous to the preceding ones were conducted on Apple and on Tomato.

Against Apple scab: A controlled test was set with 5% and 7% Cu agents. The dosages were 600 and 200 g/100 dm^3, respectively, and five treatments were conducted. Both products exhibited certain control over scab, however slightly inferior to that of the standard cupric product (oxychloride). However, a certain phytotoxicity was highlighted both on leaves and on fruits (small reddish spots), not emerging in the latter treatments. These products against scab are therefore recommendable in biological agriculture, where numberless treatments with sulfur and copper at elevated dosages are usually conducted, with high environmental and toxicity risks.

Against Tomato downy mildew: a controlled test with 5% and 7% Cu agents was set. Treatments were conducted with doses differentiated over time: the 5% Cu product was used at 300g/100 dm^3 in the first four applications and at 600g/100 dm^3 in the last two, whereas the 7% Cu product was used at 100g/100 dm^3 in the first four applications and at 200g/100 dm^3 in the last two. The results were optimal, even superior to those of the standard cupric product. Remarkably, no symptoms of phytotoxicity were highlighted.

A similar test was conducted with five treatments at the doses of 300 and 600g/100 dm^3 for the 5% Cu product and at the doses 100 and 250g/100 dm^3 for the 7% Cu product. No phytotoxicity phenomena were detected, and, moreover, an optimum disease control was attained, with an 80% average action ratio, similar to the standard product.

Example 5

Experimental tests were conducted on Hop, against downy mildew.

Against Hop downy mildew: A single treatment at 0.3% with a 3-5% Cu agent was conducted, yielding the following results.: attack ratio: 46.75% versus 73.3 and 23.96% for the untreated and the chemical product-treated theses, respectively.

Example 6

To assess the bactericide effectiveness, a test against bacterial Fire Blight (*Erwinia amylovora*) of Pear was set.

A 5% Cu agent was initially used at 600 g/100 dm^3, then at 250 g/100 dm^3, whereas a 7% Cu agent at 250 and then at 100 g/100 dm^3, with 7 treatments, was used. The observations carried out suggested an effective post-harvest autumn use, as a preventive protection and with winter and early spring “on brown” treatments, also with trunk and branch brushings.

Environmental compatibility

The abovedescribed agents have a very low content of metallic copper. Hence, in every treatment, as a function of the crops and of the phenological period, the copper quantity that would be applied onto the crops via the traditional cupric products is remarkably reduced.

This determines: a significant reduction in the environmental contamination, mostly of soil; a reduction in the negative effects towards the sequential cropping and a next to nil impact onto soil microflora and useful insects and mites.

Conclusions

The abovedisclosed agents, based on copper complexes and chelates with amino acids and/or peptides, besides providing a satisfactory effectiveness against plant diseases commonly cured with cupric products (e.g.: Downy mildew), can also be used against diseases like the *Botrytis*, the Scab, the Rusts (*Puccinia*), *Pythium*, *Fusarium,* etc.

The effectiveness of these agents is not always comparable to that of the synthetic chemical products, yet it is directly comparable to that of other traditional cupric products. Unlike the latter, the action of the former becomes evident at markedly lower copper doses (on average, 1/4-1/5) rendering applications less polluting and therefore into line with modern views, tending to minimise copper applications.

This renders said agents, based onto a completely different philosophy, aimed at environmental and health preservation rather than at attaining a 100% effectiveness of the products, particularly suitable for biological agriculture,.

Another possible use could be in view of an integrated fight, with initial applications of synthetic products (mostly against Grape mildew) followed by treatments with the peptides.

A particularly interesting aspect of such applications is the possibility of phytotoxic effects differentiated, besides from doses, according to the crops, the cultivar and the periods of use,. However, to date, in the experimental tests conducted, at the normal use doses, the phenomenon, though visible at times, did not markedly affect production.

* * *

To the above described fungicide and bactericide agent a person skilled in the art, in order to satisfy further and contingent needs may effect several further modifications and variants, all however falling within the protective scope of the present invention, as defined by the appended claims.

CLAIMS

1. A copper-based fungicide and bactericide agent, characterised in that it comprises amino acids or peptides or a mixture thereof obtained from waste or from products of animal, or vegetal, or synthetic origin with an effective quantity of copper.

2. The agent according to claim 1, wherein said effective quantity of copper is obtained starting from one or more copper compounds.

3. The agent according to claim 2, wherein said one or more copper compounds comprises copper sulphate, copper carbonate, copper oxide, copper hydroxide and mixtures thereof.

4. The agent according to claim 1, provided in a liquid or in a powdery formulation.

5. The agent according to claim 1, wherein said effective quantity of copper, preferably in bivalent form, comprises salts of amino acids, of peptides, or of mixtures thereof, or copper complexes and chelates therewith.

6. The agent according to claim 1, wherein the copper concentration is ≤40%.

7. The agent according to claim 6, wherein said concentration is ≤20%.

8. The agent according to claim 1, wherein the amino acids and/or the peptides derive from the hydrolysis of waste or products of animal or vegetal origin.

9. The agent according to claim 8, wherein said waste or products of animal or vegetal origin are charged with individual free amino acids or mixtures thereof.

10. The agent according to claim 1, wherein amino acids or peptides or amino acids and peptides obtained by synthesis or fermentation.

11. The agent according to claim 10, wherein said amino acids and/or peptides have a <2000 dalton average molecular weight.

12. The agent according to claim 1, completely miscible and soluble in water.

13. The agent according to claim 1, having, in a 10% solution, a pH ranging from 2 to 9.

14. An use of agents according to any one of the claims 1 to 13, foliar, by in-soil treatment, or by direct bulb dipping.

15. The use of agents according to any one of the claims 1 to 13, by dissolving in the irrigation waters; or by pre-transplant bulb dipping.

16. The use of agents according to any one of the claims 1 to 13, optionally in combination with one or more chemical products.

17. The use of agents according to claim 16, wherein said chemical products comprise cupric and/or sulfur-based products.

18. The use of agents according to any one of the claims 1 to 13, dissolved in

water in a concentration ranging from 0.05% to 10% (from 50 g to 10 kg in 100 dm^3 H_20).

INTERNATIONAL SEARCH REPORT

Inter al Application No
PCT/IT 01/00425

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N59/20 //(A01N59/20,61:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 13552 A (TATE DAVID) 19 September 1991 (1991-09-19) the whole document	1,2,4-18
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X	FR 2 777 193 A (COLETICA) 15 October 1999 (1999-10-15) example 11	1-13
X	WO 96 23635 A (COMMW SCIENT IND RES ORG ;MAMERS HEIKKI (AU); MCCARTHY KEVIN JAMES) 8 August 1996 (1996-08-08) the whole document	1-13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bertrand, F

Inter Application No
PCT/IT 01/00425

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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